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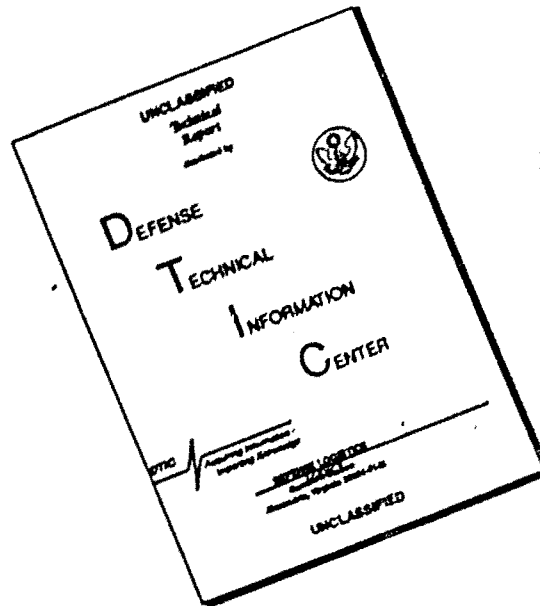*by the*

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FIFTH BIMONTHLY PROGRESS REPORT

Covering the Period

1 December 1961 to 31 January 1962

TITLE: ACCELERATED DETERIORATION OF TEXTILES

Prepared By

Charles A. Rader and Anthony M. Schwartz

Date: 15 February 1962

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INTRODUCTION AND RELATIONSHIP TO PREVIOUS WORK

It was demonstrated in the previous report of this series that the presence of ferric ion in cellophane causes an increase in the rate of its photodegradation on exposure to light in the Fadeometer. In these studies degradation was determined in sheets of cellophane exposed for periods up to 150 hours in the Fadeometer. Degradation has now been determined in sheets of cellophane exposed for times up to 300 hours, as reported herein.

Some experiments with photodegradation catalysts for cellulose other than ferric ion have been described in previous reports of this series. The study of additional new photodegradation catalysts has been extended in the current report period.

Also described in this report are initial experiments with photodegradation catalysts for nylon.

SUMMARY

Sheets of cellophane containing 0.87% ferric nitrate (0.2% ferric ion), were prepared by impregnating the cellophane with its own weight of a 0.036 molal solution of ferric nitrate. Sheets of this treated cellophane and untreated cellophane were exposed to light in the Fadeometer for periods up to 300 hours. Degradation of the cellophane was measured by loss in breaking strength and also by reduction in viscosity, which was calculated to degree of polymerization (DP). As observed previously with samples exposed for periods up to 150 hours, the treated cellophane was degraded more than the untreated in every case where the samples were exposed for the same length of time. It was found that the treated cellophane suffered a complete loss in tensile strength when exposed for 300 hours. As reported previously the treated cellophane lost about 25% of its original strength after 150 hours Fadeometer exposure. The reduction in

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DP after 300 hours exposure was only slightly greater than that after 150 hours exposure, but apparently at the lower DP produced by longer exposure, the cellulose chains were no longer able to form a cohesive sheet.

This result suggests that, in a cotton fabric, significant changes in abrasion resistance, tearing strength, and physical properties other than breaking strength might also be achieved with correspondingly lesser changes in the DP of the cotton. This hypothesis will be checked by extending the present studies with photodegraded cotton to include various physical tests in addition to the determination of breaking strength. DP's of the degraded cotton will be determined from the fluidities of cupraethylenediamine solutions, just as has been done with cellophane.

Work was continued using degradation accelerators other than ferric ion on cotton. Those tested were: zinc sulfide, thionin, methylene blue (tetramethyl thionin), anthracene, acenaphthene, Blancophor R (General Aniline and Film Corp.), Uvitex RS (Ciba Co.), Uvitex RT (Ciba Co.), and Seto Flavine T Supra (Geigy Dyestuffs). The last six of these compounds exhibit some fluorescence under ultraviolet light. Only one of the above compounds, acenaphthene, had a significant degrading effect on cotton. The acenaphthene was only about one-third as effective as ferric ion (as ferric nitrate or ferric chloride), however.

Several combinations of catalysts were also tested on cotton. These were: ferric ion plus thionin, ceric ion (as ceric nitrate) plus thionin, ferric ion plus 2-anthraquinone sodium sulfonate, and ceric ion plus 2-anthraquinone sodium sulfonate. The strength losses caused by the combinations containing ferric ion were no greater and in most cases were a little less than the sum of the strength losses caused by the ferric ion and organic compound, individually. The combinations containing ceric ion were much less effective than the ceric ion alone.

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Most of the catalysts tested ~~to date~~ on cotton have now been tested on nylon fabric. In these initial studies degradation of the nylon has been determined only as loss in breaking strength.

It was found that the untreated nylon was significantly degraded by light in the Fadeometer, suffering almost 35% strength loss after 30 hours exposure. Nylon fabrics treated with ferric nitrate and exposed for 30 hours were hardly any weaker than untreated nylon exposed for the same period. Both fabrics suffered a strength loss of 30 to 30%. When the fabrics had been exposed for only 10 hours, however, the treated fabrics were significantly weaker than the controls (25% loss as against only 8% loss). After 10 hours exposure 0.002% Uvitex RT or 0.002% Seto Flavine T Supra caused about 15-20% strength loss in the nylon, based on the exposed untreated control. These treatments were about as effective as 0.2% ferric ion, 0.2% thionin, or 0.2% acenaphthene. It is interesting that some of the fluorescent compounds, relatively ineffective on cotton, were effective degradation accelerators on nylon.

FUTURE WORK PLANNED

1. The study of degradation accelerators for cellulose and nylon will be continued.

2. Degradation of the woven fabrics will be determined as changes in tearing strength, abrasion resistance and other properties as well as loss in breaking strength.

DETAILS

Materials and Apparatus

The cellophane and cotton used in these studies were the Avisco Type 300 cellophane and the 80 x 80 printcloth described in previous reports of this series. The nylon used was a filament taffeta, type 200, bright (from Test-fabrics, Inc. - Stock No. 302A). Before being used in these studies it was

laundered in 0.1% Triton X-100 and thoroughly rinsed in water. One by six inch die-cut strips (six inches in the warp direction) of the untreated laundered nylon, conditioned at 70° F., 65% R.H., had breaking strengths of 102 ± 2 lbs.

Samples were exposed to light in the Fadeometer at an ambient air temperature of 44 ± 3° C., as previously described. For all of the experiments described below the light intensity incident on the samples in the Fadeometer was 1.85 ± 0.20 x 10^{-4} mole of light per hour per square centimeter. The technique for measuring light intensity, using uranyl oxalate actinometers, has been described in the Second Bimonthly Report.

In all of the experiments described below the compound being studied for its photodegradative effect on cotton or nylon was applied to the fabric from a solution. (Zinc sulfide was precipitated in situ on cotton by applying zinc acetate and sodium sulfide solutions.) Water was used as the solvent in most cases; where a compound was not soluble in water, an appropriate volatile organic solvent was used. The solutions were applied dropwise from a pipet to the fabric swatches, the weight of solution applied being exactly equal to the weight of dry fabric (100% wet pick-up). The treating solutions used are listed in Appendix A. Their concentrations are given expressed on a weight percent basis, and on a molal basis. Throughout the main body of the report the amount of catalyst on fabric is expressed as a weight percent add-on.

Degradation of Cellophane

Sheets of untreated cellophane and cellophane containing 0.2% of ferric ion (as ferric nitrate) were exposed in the Fadeometer for periods of 32 hours and 300 hours. The preparation of these samples has been described in the Fourth Bimonthly Report. Losses in breaking strength, and the DP's determined from the viscosities of cupraethylenediamine (CUENE) solutions for these samples

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are given in Table 1. Also included in Table 1 are data from the Fourth
Bimonthly Report for unexposed samples and for samples which had been exposed
for times of 30, 100, and 150 hours.

The ferric ion was extracted from the treated cellophane with 0.1N HCl
before the cellophane was dissolved in CUENE. As reported previously the HCl
probably causes a slight reduction in DP. Several examples of the effect of
HCl on untreated exposed cellophane are given in Table 1.

Degradation of Cotton Fabrics

Table 2 lists the degradation accelerators which were investigated on
cotton. Breaking strength losses for samples exposed in the Fadeometer and for
samples stored at 70° F., 65% R.H. under ordinary indoor illumination are given.
In every case approximately 48 hours elapsed between the time the samples were
treated and the time they were broken. The samples which were exposed in the
Fadeometer for 30 hours were stored at 70° F., 65% R.H. for the remainder of
the 48 hours.

Acenaphthene was the only one of the group of ultraviolet fluorescent
compounds which effected a significant amount of photodegradation. As shown
in Table 2 it was far less effective than ferric ion.

The presence of thionin or 2-anthraquinone sodium sulfonate did not
increase the effectiveness of ferric ion, and these compounds actually decreased
the effectiveness of ceric ion.

Degradation of Nylon Fabrics

The effects of varying times of exposure in the Fadeometer on untreated
and treated nylon fabrics are shown in Table 3. There appears to be an appreciable
"dark" reaction between ferric ion and nylon. Further degradation of the nylon
occurs on exposure to actinic light, but this rate of photodegradation slows to
such an extent after the first few hours that the treated nylon is only slightly
more degraded than untreated nylon after 30 hours. Similar slow rates of photo-
degradation were observed with other catalysts. Thus, in order to better

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differentiate between the effects of the various catalysts, 10 hours was selected as a standard exposure time for screening most of the treated nylon fabrics.

Table 4 lists the degradation accelerators which were investigated on nylon. Breaking strength losses for samples stored at 70° F., 65% R.H. and for samples exposed in the Fadeometer are given. Several of the compounds exhibiting fluorescence under ultraviolet illumination accelerated the photo-degradation of nylon. Thionin, which absorbs light strongly only in the visible region at about 600 millimicrons, was also effective.

Tables 2 and 4 demonstrate the relative ease of photodegradation of nylon, in comparison with cotton. According to recently published studies the nylon polymer chains are probably cleaved at a carbon-nitrogen bond (bond energy equals 66 kcal per mole) (Refs. 1 and 2). The cellulose is cleaved at a carbon-oxygen bond (bond energy 78 kcal per mole) (Ref. 3). Light at wave lengths shorter than 420 millicrons possesses enough energy to break a carbon-nitrogen bond, but only wave lengths shorter than 360 millimicrons possess energies greater than 78 kcal per mole.

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TABLE 1

PHOTODEGRADATION OF CELLOPHANE IN THE PRESENCE AND ABSENCE OF FERRIC ION

Hours Exposed in Fadeometer*	Ferric Ion Concentration, %	Loss in Breaking Strength, %	D.P. Before Extraction with HCl	D.P. After Extraction with HCl
0	0	0	350 to 370[a]	362
0	0.2	0	Not tested	288
30	0	0	348	317
30	0.2	14	Not tested	195
32	0	0	345	314
32	0.2	10	Not tested	195
1C0	0	6	328	Not tested
100	0.2	17	Not tested	185
150	0	6	266, 268[b]	Not tested
150	0.2	25	Not tested	148
300	0	Not tested	253	232
300	0.2	100[c]	Not tested	119

* - Ambient air temperature was 44° C.

a - Range for 5 sheets, D.P.'s determined on different days.

b - Two separate sheets, exposed at different times.

c - Cellophane was friable, too weak to handle.

TABLE 2

PHOTOCATALYTIC DEGRADATION OF COTTON

Catalyst, % on Fabric	Percent Strength Loss	
	Stored at 70°F., 65% RH	Exposed 30 hours in the Fadeometer
None	0	7
Ferric ion[a], 0.1%	20	58
*Ceric ion[b], 0.1%	7	34
Thionin, 0.2%	3	8
Thionin, 0.2% plus ferric ion[a], 0.1%	23	65
Thionin, 0.2% plus ceric ion[b], 0.1%	10	17
2-anthraquinone sodium sulfonate, 0.2%	3	21
2-anthraquinone sodium sulfonate, 0.2% plus ferric ion[a], 0.1%	28	63
2-anthraquinone sodium sulfonate, 0.2% plus ceric ion[b], 0.1%	0	14
Methylene blue, 0.2%	0	5
Acenaphthene, 0.2%	3	20
Anthracene, 0.2%	2	0
Blancophor R, 0.002%	6	6
Uvitex RS, 0.002%	8	5
Uvitex RT, 0.002%	10	9
Seto Flavine T Supra, 0.002%	8	9
Zinc Sulfide, 0.1%	0	10

* - Taken from Table 2 of the Fourth Bimonthly Report.
a - Applied as ferric nitrate.
b - Applied as ceric nitrate.

TABLE 3

EFFECT OF EXPOSURE TIME ON PHOTOCATALYTIC DEGRADATION OF NYLON

Catalyst, % on Fabric	Percent Strength Loss from Untreated Unexposed Nylon			
	Stored at 70°F., 65% RH	Exposed in Fadeometer		
		5 hrs.	10 hrs.	30 hrs.
None	0	3	8	30
Ferric ion[a], 0.2%	13	27	29	35
Thionin, 0.2%	0	11	25	40

a - Applied as ferric nitrate.

TABLE 4

PHOTOCATALYTIC DEGRADATION OF NYLON

NT indicates not tested

Catalyst, % on Fabric	Percent Strength Loss, Based on Untreated Control		
	Stored at 70°F., 65% RH	Exposed in Fadeometer 10 hrs.	30 hrs.
None	0	8*	30*
Ferric ion[a], 0.1%	7	NT	4
Ferric ion[a], 0.2%	13	20	8
Ceric ion[b], 0.1%	11	NT	15
Cerous ion[c], 0.1%	0	NT	6
Thionin, 0.2%	0	17	15
Thionin, 0.2% plus ferric ion[a], 0.1%	4	NT	21
Acenaphthene, 0.2%	0	14	15
Anthracene, 0.2%	5	3	10
1-anthraquinone sodium sulfonate, 0.2%	0	0	0
2-anthraquinone sodium sulfonate, 0.2%	0	0	3
Blancophor R, 0.002%	8	11	NT
Uvitex RS, 0.002%	2	0	NT
Uvitex RT, 0.002%	2	15	NT
Seto Flavine T Supra, 0.002%	6	18	NT

* - Based on unexposed nylon.
a - Applied as ferric nitrate.
b - Applied as ceric nitrate.
c - Applied as cerous chloride.

APPENDIX A

Solutions of Compounds Studied as Photodegradation Accelerators on Cotton and Nylon

Compound	Solvent	Concentration % by Weight	Molal
Ferric nitrate	0.001N HNO$_3$	0.43 (0.1 ferric ion)	0.018
Ferric chloride	0.001N HCl	0.29 (0.1 ferric ion)	0.018
Ceric nitrate	95% ethanol	0.28 (0.1 ceric ion)	0.0071
Zinc acetate	Water	0.18 (0.067 zinc)	0.010
Sodium sulfide	Water	·0.08 (0.033 sulfur)	0.010
Acenaphthene	95% ethanol	0.2	0.011
Thionin	95% ethanol	0.2	0.0088
Methylene Blue	Water	0.2	0.0054
2-anthraquinone sodium sulfonate	Water	0.2	0.0065
Anthracene	Chloroform	0.2	0.011
Blancophor R	Water	0.002	3×10^{-5}
Seto Flavine T Supra	Water	0.002	6×10^{-5}
Uvitex RS	Water	0.002	8×10^{-5}
Uvitex RT	Water	0.002	*

* - Molecular weight of Uvitex RT not available.